

PREPARATION OF ADHESIVE USING SOY PROTEIN AND LIGNIN

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ABSTRACT

Abundant, renewable and inexpensive soybean can be a good alternative to natural adhesive. Soy flour was modified by repeated digestion of soy flour by sodium hydroxide and hydrochloric acid. 5%, 10% and 20% modified soy flour (MSF) was then prepared. Medium density fibreboard (MDF) of 810 kg/m³ was made using wood fibre and thickness swelling properties and mechanical properties were analyzed to determine the performance of the board. In the second part, the MSF concentration with the best mechanical result was used to prepare MSF with enzymatic hydrolase lignin (EHL) of that particular concentration. Laccase enzyme was added to 5% lignin to produce EHL. Thickness swelling and mechanical properties were analyzed to determine the performance of the board. FTIR and DSC analysis were performed to understand the structure and properties of all the different types of adhesive. Thickness swelling test exhibit that 5% MSF showed the least thickness swelling. However it did not meet the requirement of ASTM. 10% MSF with EHL did not show a better result either as it increased to more than 100%. For mechanical testing, internal bonding for 10% MSF showed the best result and it almost reached the ASTM standard. 10% MSF with EHL also showed similar result as the 10% modified soy flour. As for modulus of rupture, 10% MSF also had better results. However, both 10% MSF and MSF with lignin had results that were passing the ASTM standard.

ABSTRAK

Kacang soya yang banyak, boleh diperbaharui dan murah boleh menjadi alternatif yang baik untuk pelekat semula jadi. Tepung soya telah diubahsuai dengan berulang tepung soya penghadaman oleh natrium hidroksida dan asid hidroklorik. 5%, 10% dan 20% tepung soya yang diubahsuai (MSF) disediakan kemudian. Papan gentian ketumpatan sederhana 810 kg/m³ dibuat menggunakan serat kayu dan harta Dalam bahagian kedua, tumpuan MSF dengan keputusan mekanikal yang terbaik telah digunakan untuk menyediakan MSF dengan lignin hydrolase enzim (EHL) tumpuan yang tertentu bengkak ketebalan dan sifat mekanik telah dianalisis untuk menentukan prestasi papan. Laccase enzim ditambah kepada 5% lignin untuk menghasilkan EHL. Bengkak ketebalan dan sifat mekanik telah dianalisis untuk menentukan prestasi lembaga. Analisis FTIR dan DSC telah dijalankan untuk memahami struktur dan sifat-sifat semua jenis pelekat. 5% MSF menunjukkan bengkak ketebalan yang paling kurang. Walau bagaimanapun ia tidak memenuhi keperluan ASTM. 10% MSF dengan EHL juga tidak menunjukkan keputusan yang baik kerana ia meningkat kepada lebih daripada 100%. Untuk ujian mekanikal, ikatan dalaman 10% MSF menunjukkan hasil yang terbaik dan ia hampir mencapai standard ASTM. 10% MSF dengan EHL juga menunjukkan hasil yang sama seperti 10% MSF. Bagi modulus pecah, 10% MSF juga mempunyai keputusan yang lebih baik. Walau bagaimanapun, kedua-dua 10% MSF dan MSF dengan lignin mempunyai keputusan yang memenuhi standard ASTM.

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LIST OF SYMBOLS AND UNIT

°C	celcius
cm	centimetre
g	gram
kDa	kilo Dalton
kg	kilogram
MPa	megapascal
mg	milligram
min	minute
ml	millilitre
mm	millimetre
h	hour
m.w	molecular weight
M	molarity
N	normality
rpm	revolution per minute
U	unit

LIST OF ABBREVIATIONS

3D	Three dimensional
7S	β -conglycinin
11S	Glycinin
AMSP	alkali-modified soy protein
ASTM	American Society for Testing and Materials
DSC	Differential Scanning Calorimetry
EHL	enzyme hydrolase lignin
ESL	extruded sorghum lignin
FTIR	Fourier Transform Infrared
GH	Guanidine Hydrochloride
HCl	Hydrochloric acid
IB	Internal Bonding
LVL	Laminated venner lumber
MDF	Medium Density Fibreboard
MOE	Modulus of Elasticity
MOR	Modulus of Rupture
MSF	Modified soy protein
N	Normality
NaOH	Sodium hydroxide
OSA	2-octen-1-ylsuccinic anhydride
OSB	Oriented Strandboard
PAE	polyamidoamine-epichlorohydrin
PF	Phenol-Formaldehyde
SDS	Sodium Dodecyl Sulfate
SDBS	Sodium Dodecylbenzene Sulfate

SL	Sorghum lignin
SPI	Soy Protein Isolate
TMSP	Trypsin Modified Soy Protein
UF	Urea-Formaldehyde
U-SPI	Urea Soy Protein Isolate

CHAPTER 1

INTRODUCTION

1.1 Motivation

Over the past 75 years, the source for wood adhesives has dramatically changed. For centuries, natural adhesives have been used to make products. Since the early days, adhesive was used to glue wood veneer to furniture. Nowadays, they are used in application such as assembling furniture and in roof beams. Back in the days, soy protein based adhesive was widely used where the protein was mainly taken from animals and plants (Mcgraw-Hill Yearbook of Science & Technology, 2010).

However, due to the easiness to convert into well-defined, uniform and specifically designed polymers, fossil fuels have made a prominent role in replacing soy protein adhesive. Adhesive was shift to petroleum-based adhesives as they have better glueing strength, water, heat, moisture and decay resistance, making it a better choice as adhesive in the wood market. Another factor that contribute to this shift was because of the decreased in petrochemicals cost (Mcgraw-Hill Yearbook of Science & Technology, 2010).

Moving forward 75 years later, its use has been touted as not environmental friendly and resulted in unfavourable environmental issues in addition to poor waste management, harmful effects on human's health and the hiked in prices and the desire to turn to greener and more environmental friendly products have led people to revert back to adhesive made from soy protein-based ones. In the desire to produce and come out with a more environmental friendly adhesives, researches need to come out with better and suitable technologies. Moreover, the increase need for low-cost adhesives with enough supply and durability were also the factors that contribute to the effort to replace petrochemically based adhesives.

For soy protein, it is vital to understand the structure and the key components that lead to good adhesive properties. Proteins are different from other adhesives in terms of their structure and property relationships. Protein is modified to improve the structure of native

soybean proteins which are a highly ordered global structure with the hydrophilic groups being exposed on the outside while the hydrophobic groups are buried on the inside. Hydrogen bonds which prevent the reactive group from interacting with the wood substrate can be broken by making modifications to its functional properties at the secondary, tertiary and quaternary levels by changing its molecular structure by physical, chemical means or by enzymatic reaction. These modifications will cause the internal hydrogen bonds to break resulting in the unfolding of the protein molecules thus making the reactive structure to react with cellulosic materials and increase its adhesion properties (Mo et al., 2004). Zhong et al. (2003), Huang and Sun (2000), Hettiarachchy et al. (1995) and Sun and Bian (1999) are some of the researches that have studied the properties of soy protein by modifying it by adding alkali, trypsin, sodium dodecyl sulfate, guanidine hydrochloride and sodium dodecylbenzene sulfonate.

Lignins on the other hand are mainly recovered as byproducts from wood pulping operations where around 75 million tons are annually produced worldwide. (Petrie, 2012). They are the components that hold the plant fibres together. This particular property has roused interest for lignin to be used as a good wood adhesive which are non-toxic and more environmental friendly. Lignin being a renewable, non-toxic, easily available and low cost material has seen in recent years being used in the development of thermosetting resins used as wood adhesive. They are used to substitute part of phenol-formaldehyde or urea-formaldehyde resins. Olivares et al. (1988) used lignin as a copolymer in lignin-phenol-formaldehyde resin binders while Mancera et al. (2011) have used lignin as an adhesive to manufacture *Vitis vinifera* fibreboard and they obtained good mechanical and water resistance properties that satisfied the relevant standard specifications.

Although soy protein and lignin have their own characteristics and potentials to be good adhesive, there are hardly any research being done on producing adhesive using these two components. In Malaysia, since they can be easily obtained and are cheap, producing adhesive through this method would be another great way in producing a greener and environmental friendly adhesive. Moreover, the long-term outlook for supply and price stability in the oil market are also a concern and composite wood product manufacturers are eager to find a more reliable source and better ways to produce adhesive using better and lasting technologies.

1.2 Problem Statement

1.2.1 Health and Environmental Issues

In 2004, the International Agency for Research on Cancer classified formaldehyde as a potential carcinogen. (IARC, 2004). A carcinogen is a chemical capable of causing cancer. Exposure to low levels of formaldehyde aggravate the eyes, nose and throat and causing allergies that will affect the skin and lungs. Excessive and increased exposure levels can result in throat spasms and a build up of fluid in the lungs which may lead to death. Contact can also cause severe eye and skin burns, leading to permanent damage. Hours after exposure, these symptoms normally appear, even though no pain is felt. Formaldehyde can cause an asthma-like respiratory allergy. Further exposure can cause asthma attacks with shortness of breath, wheezing, cough and chest tightness. Repeated exposures may cause bronchitis, with coughing and shortness of breath.

In terms of environmental issues, formaldehyde dissolves easily in water, and eventually disintegrate. Formaldehyde decomposes in air within 24 hours to form formic acid and carbon monoxide. Formaldehyde does not bioaccumulate in plants and animals. Animals will have chronic effects including shortened lifespan, reproductive problems, lower fertility and changes in appearance or behaviour. Chronic effects can only be seen a long time after the first exposure to a toxic chemical. Formaldehyde poses danger and has high chronic toxicity to aquatic life. Apart from that, it may cause cancer and other chronic illnesses in rodents while exposure of birds and terrestrial animals to formaldehyde could contract similar diseases. (National Protection Agency, 2000).

1.2.2 Non-Renewable Raw Materials

The raw materials for making Urea-formaldehyde and Phenol-formaldehyde resins are derived from natural gas and petroleum which are non-renewable sources. The finite reserve and expanding consumption of petroleum and natural gas will definitely affect the availability of the raw materials for making these formaldehyde-based adhesives in the long run.

1.3 Objective

This research was done in order to achieve the following objectives:

1. This work aims to produce medium density fibreboard adhesive using soy protein and lignin with better adhesion, mechanical properties and water resistance.
2. Prepare adhesive which are less harmful towards the environment and human health.

1.4 Scope of Study

The scope of the research listed below is needed to achieve and accomplish the objectives:

1. Make and produce medium density fibreboard using the modified soy flour and soy-lignin adhesive.
2. The properties of medium density fibreboard produced using modified soy flour and combination of soy protein and lignin adhesive will be studied.
3. The effect of different concentration of modified soy flour as adhesive will be studied.
4. The effect of adding enzyme hydrolase lignin to the modified soy flour will be studied.
5. Mechanical testing of the medium density fibreboard will be carried out to determine the properties of the board.
6. Chemical analysis will be done on the adhesive to determine its properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

In this chapter, information regarding and related to this research will be further explained. There are many researches who have studied different ways to make and produce a good wood adhesive using soy protein. These researches have a similar goal in mind which is to find ways to replace the petroleum-based adhesive in a move to contribute to a greener environment. These improvements are usually done by changing the physical and chemical structure of the soy protein through adjustment of the pH, thermal treatment, high pressure, hydrolysis and others.

2.2 Wood Adhesive

2.2.1 Introduction

Wood adhesives are substances used for binding wood to itself or onto other materials. There have been various types of substances that were used historically for bonding wood, but until the late 1940s these adhesives were all made of natural materials . After World War II, synthetic wood adhesive started to appear and has surpassed natural glue for wood binding in modern times. Basically, wood adhesive can be placed into two distinct categories – natural and synthetic. Animal, vegetable, casein, soybean and blood glues are known as natural wood adhesive while petroleum, gas, coal and other synthetic resins are the derivation of synthetic wood adhesives (Mcgraw-Hill Yearbook of Science & Technology, 2010).

2.2.2 Natural Wood Adhesive

2.2.2.1 Animal Glue

Animal glue or also known as hot glue, is made from the hide and bones of cattle, sheep and horses. The low moisture resistance in animal glue will cause the bond to weaken when it is exposed to high humidity. Therefore, it must be applied to wood when it is still hot in order for it to form a strong bond when it cools and loses moisture. The wood should also be kept warm during application in order to prevent the glue to cool too fast thus preventing strong bonds to form. The protein in the animal glues contains a high amount of an amide group (-CONH-), free amino groups (-NH- and -NH₂) and a carboxylic acid group (-COOH). These functional groups interact with one another within and between protein chains in addition to interacting with the wood (Pernollet, 1985). Through these interactions, strength of animal glues and the adhesion is provided for. Proteins in different animal glues have different structures and consists of different amounts of these functional groups. Therefore, different animal glues have properties that vary significantly.

2.2.2.2 Vegetable Glue

According to Charles (1991), vegetable glues are glues that are produced by plants. These materials are dispersible or soluble in water and are usually made from the starches that comprises of many grains and vegetables. The natural gums include agar which is from colloids in marine plants, algin derived from seaweed and gum arabic which is an extract of the acacia tree or also known as gum tree. The substance called marine glue is used to caulk seams. However, it consists of tar or pitch which is not truly a glue.

2.2.2.3 Casein Glue

The use of casein in the gluing of wood is reported to be a very ancient art. European craftsmen understood a method of gluing with a crude casein (possibly the curd of soured milk mixed with quick lime) in the Middle Ages, and the art continued in a small way to the modern days. The manufacture of casein glue as a separate industry, however, seems to have started in Switzerland or Germany in the nineteenth century. In the United States casein glues were not popular and is used only to a very limited extent until the year 1916 or 1917, where the need for a water-resistant glue for the construction of military aircraft suddenly aroused interest in casein glue and promptly led to its extended production and use. The main ingredient of casein glue is casein, which is the chief protein essential to milk. When milk

becomes sour, it will separate into curd and whey. The curd, when washed and dried, is the casein of commerce. When made in this way, it is known as self-soured or naturally soured casein. Casein is also precipitated by mineral acids, such as hydrochloric or sulfuric, and by rennet. In preparing the glue, caseins precipitated by the different methods will require different amounts of water to produce solutions of similar viscosity. The degree and type of alkali influences product behaviour. Satisfactory glues, however, can be produced from caseins precipitated by any of these methods provided the casein is of good quality. In wood bonding, casein glues generally are superior to true animal glues in moisture resistance and aging characteristics (Charles, 1991).

2.2.2.4 Blood Glue

Blood glues are used in much the same manner as casein glues. The proteins from animal blood in slaughtering are precipitate out, dried and sold as powders which are then mixed with water, hydrated lime or sodium hydroxide. Blood glues are used to a limited extent in making softwood plywood, sometimes in combination with casein or soybean proteins. They have also been used as extenders for phenolic-resin glues for interior type softwood plywood. Blood-based adhesives have a higher moisture resistance, but it is still lower strength than casein-based adhesive (Charles & William, 1963).

2.2.2.5 Soybean Glue

2.2.2.5.1 Composition of Soybean

Major storage proteins of soybean are globulins. There are four protein fractions that are classified according to their sedimentation properties. They are 2S, 7S, 11S and 15S fractions and comprise 8%, 35%, 52% and 5% of the total protein content respectively. The principal storage proteins are glycinin (11S) and β -conglycinin (7S) and constitute over 70 % of soluble protein. Their content, ratio and dynamics of biosynthesis vary with soybean varieties and environment (Murphy, 1984). According to Staswick, Hermodson and Nielson (1984), glycinin (m.w ~360 kDa) is a protein with compact quaternary structure stabilized via disulfide, electrostatic and hydrophobic interactions. It is made up of six A-SS-B subunits. Each subunit is composed of an acid (m.w. ~38 kDa) and basic polypeptide (mw ~20 kDa) linked by single disulfide bond, except for the acid polypeptide -A4-. Subunits are packed into

two hexagons placed one over the other to form a hollow oblate cylinder. β - Conglycinin is a major protein of 7S fraction with molecular weight of 150 -180 kDa (Thanh & Shibasaki, 1976). It is composed of three subunits, α' -, α - and β - which interact to produce seven isomers (B0-B6). Molecular weight of these subunits is 72 kDa, 68 kDa and 52 kDa, respectively. The original β -conglycinin is a glycoprotein and it contains the carbohydrates as one unit attached to the aspartic acid residue at the N-terminal end of the molecule. The carbohydrate moiety consists of 38 mannose and 12 glucosamine residues per molecule of protein. Due to the different structure, there are a number of physicochemical differences in the 7S and 11S protein components. For example, 11S protein is insoluble at pH 6.4 and 2-5°C, whereas β -conglycinin is insoluble at pH 4.8. The literature contains numerous references that describe the physicochemical and functional properties of these proteins and their subunits.

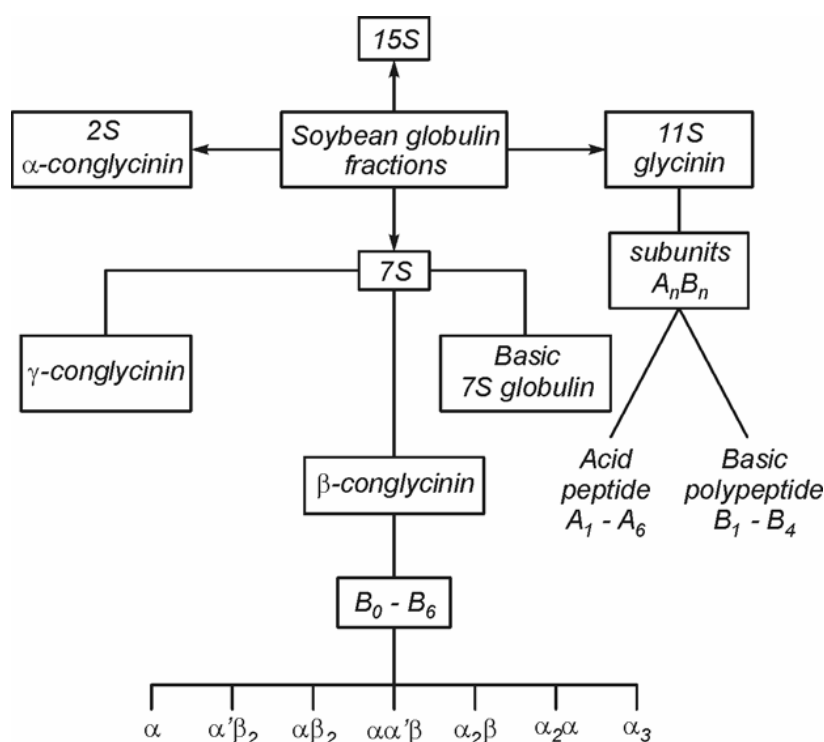


Figure 2.1: Soybean composition

2.2.3 Synthetic Adhesive Derived from Petrochemicals

Petrochemicals are used to produce two types of synthetic resins: thermosetting resins and thermoplastic resins. After being heated at a certain temperature, thermosetting resins become insoluble and infusible materials resulting into an irreversible process. As for thermoplastic resins, they soften or melt when being heated and solidify again when being cooled. The process of softening and solidifying are reversible and can be repeated many times (Eckelman, 1997).

2.2.3.1 Urea-Formaldehyde Resins

Urea-formaldehyde (UF) resins are the most prominent examples of the class of thermosetting resins usually referred to as amino resins.^{2,3} Urea-formaldehyde resins comprise about 80% of the amino resins produced worldwide. (Skeist, 1990, p. 341).

Urea-formaldehyde resins are formed by the reaction of urea and formaldehyde. The overall reaction of urea with formaldehyde has initially been studied early in the century. However, due to its complexity, it is still yet to be completely understood at the present time. (Pizzi, 1983). The synthesis of a urea-formaldehyde resin takes place in two stages. In the first stage, urea is hydroxymethylolated by the addition of formaldehyde to the amino groups. This reaction is a series of reactions that lead to the formation of mono-, di-, and trimethylolureas. Tetramethylolurea is apparently not produced, at least not in a detectable quantity. The addition of formaldehyde to urea takes place over the entire pH range. The reaction rate is dependent on the pH. The rate for the addition of formaldehyde to successively form one, two, and three methylol groups has been estimated to be in the ratio of 9:3:1 respectively. The exact ratio, of course, is dependent on the reaction conditions employed in the addition reaction. The second stage of urea-formaldehyde resin synthesis consists of the condensation of the methylolureas to low molecular weight polymers. As mentioned, the rate at which these condensation reactions takes place is highly dependent on the pH and, for all practical purposes, occurs only at acidic pHs. The increase in the molecular weight of the urea-formaldehyde resin under acidic conditions is thought to be a combination of reactions leading to the formation of methylene bridges between amido nitrogens by the reaction of methylol and amino groups on reacting molecules; methylene ether linkages by the reaction of two methylol groups; methylene linkages from methylene ether linkages by the splitting out

of formaldehyde; and methylene linkages by the reaction of methylol groups splitting out water and formaldehyde in the process. The difference between the pH profiles of the two stages of urea-formaldehyde resin synthesis is used to advantage in the production of urea-formaldehyde adhesive resins. (Anthony & Alfred, 1995).

As a wood adhesive, urea-formaldehyde resins are advantageous because they are inexpensive, have good processing and curing properties, and are resistant to fungi and termites. (Meyer, 1979). Greater utilization of urea-formaldehyde resins is impeded, however, because of the emission of formaldehyde which may result in potential health hazards and environmental pollution. (Coutrot, 1986).

2.2.3.2 Phenol-Formaldehyde Resins

Phenol-formaldehyde (PF) are extensively employed as bonding adhesives in the manufacture of composite wood panels, imparting the water resistance required for exterior application such as roofs and external house walls. They are mainly the products of the reaction between phenol and formaldehyde which is catalysed by alkali to provide a thermosetting polymer called resole. (Athanassiadou et al., 2010).

In the preparation of resoles, the molar ratio of formaldehyde to phenol is more than one. Phenol may be substituted with more than one methylol group. These substituted phenols can later react among themselves to form a mixture of polymers with different sizes and different degrees of branching. Resoles will form highly crosslinked polymer networks when cured at a higher temperature. In contrast, the formaldehyde/phenol molar ratio is less than one in the initial stage of preparing novolacs. This is because the methylol group is not stable under an acidic condition and can quickly react with phenol to form polymers. The low formaldehyde/phenol ratio allows the resulting PF resins to have relatively low molecular weight to allow them to flow and penetrate the wood. Extra amount of formaldehyde has to be added to further react the adhesive, resulting in the formation of highly crosslinked polymer networks. With the aid of special catalysts such as divalent metal acetates, phenols can be predominantly linked at ortho-positions, causing novolacs to have a linear structure. (Koch, 1987).

PF resins are mainly used for production of exteriorly used structural wood composite panels such as plywood and laminated veneer lumber (LVL) because of their good durability and

high strength even under harsh weather conditions. After curing, PF resins will have a dark color, which negatively affects the aesthetics of wood composite products. Therefore, PF resins are normally not used for production of interiorly used wood composite panels. (Skeist, 1990).

2.2.4 Lignin

2.2.4.1 Introduction

Lignin is a natural amorphous polymer. It acts as an adhesive to give plants their structural integrity. Lignin is the second most abundant and the only biomass constituent based on aromatic units out of the three major natural polymers that make up ordinary plants namely cellulose, lignin and hemicellulose (Gallezot, 2008). They are derived from trees, plants and agricultural crops and are recovered in large quantities as byproducts from pulping mills mainly in the form of kraft lignin and liginosulfonate.

2.2.4.2 Structure of Lignin

After many years of study, the structure of native lignin still remains unclear. Lignin is actually not one compound but many complex, amorphous, three-dimensional polymers that have in common a phenylpropane structure, that is, a benzene ring with a tail of three carbons. In their natural unprocessed form, none of them has ever been completely described due to its complexity, and having molecular weight reaching up to 15,000 or more. However, the dominant structures in lignin have been elucidated as the methods for identification of the degradation products and for the synthesis of model compounds have improved. The results from these numerous studies have yielded what is believed to be an accurate representation of the structure of lignin. Examples of the elucidated structural features of lignin include the dominant linkages between the phenylpropane units and their abundance, as well as the abundance and frequency of some functional groups. Linkages between the phenylpropane units and the various functional groups on these units give lignin a unique and very complex structure (Ruben et al., 2010).

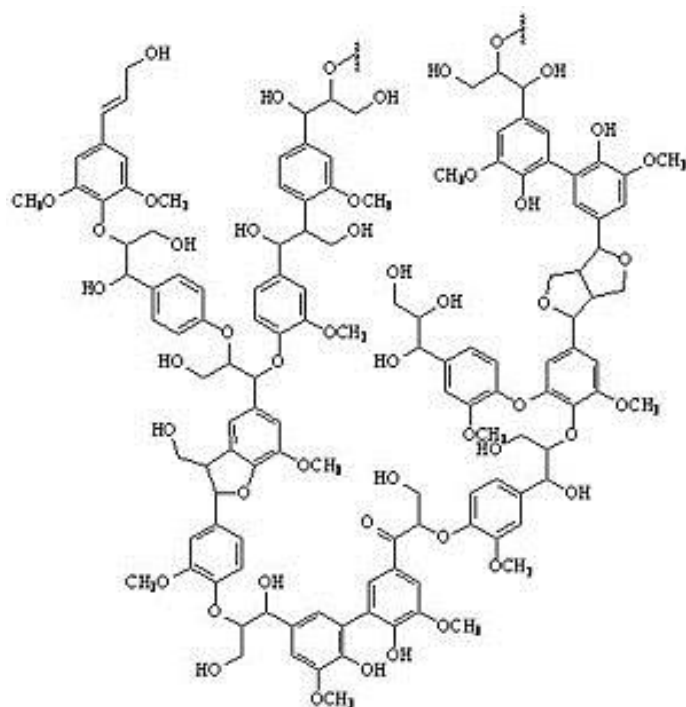


Figure 2.2: Lignin Structure

2.3 Soy Protein Adhesive

Soybean-based adhesives, commonly called soy-based adhesives were widely used in the production of wood composites from the 1930s to the 1960s. Soy-based adhesives have many advantages such as cheaper cost, easier handling and lower pressing temperature (Li et al., 2004). The renewed interest in soy-based adhesives in recent years because soybean is abundant, inexpensive, and readily available. However, wood composite panels bonded with the soy-based adhesives had relatively low strength and low water-resistance, which results in the adhesives to be replaced by formaldehyde-based adhesives.

2.4 Lignin as Adhesive

2.4.1 Introduction

Over the years, lignin has been one of the most intensely researched raw materials for wood adhesives, mainly because of its very low cost. Lignin provides biomass based resins with a phenolic-like molecular structure. Lignin is unusual as a biopolymer resulting in difficulty to adapt to adhesives as compared to starch, cellulose or soy because of its heterogeneity and inexact composition. Native lignin is a crosslinked polymer, but the polymers have to be partially degraded to allow separation from the cellulosics. These degraded lignin resins need to be further polymerized to obtain useful adhesive properties. Lignin from the pulping process does not lead to a useful product because of the cost of separating the lignin from the pulping chemicals and the variability of the product. However, lignin sulfonates, contained in the spent sulfate liquids from sulfite pulping of wood have been found to be a more useful feedstock for the production of reactive lignin. Lignin based wood adhesives have been prepared with formaldehyde or other aldehydes. There have been claimed to provide properties which are up to par with the conventional phenol formaldehyde adhesive, the quality of lignin-based resins diversify significantly depending on wood source, the pulping operation and other considerations (Petrie, 2012).

2.4.2 Production of Synthetic-Resin-Free Wood Panel Adhesives From Mixed Low Molecular Mass Lignin And Tannin

Mansouri et al. (2010) produced mixed interior wood panel tannin adhesive where lignin is in considerable proportion, 50%, of the wood panel binder and in which no "fortification" with synthetic resins, such as isocyanates and phenol-formaldehyde resins as used in the past, was necessary to obtain results satisfying relevant standards. A low molecular mass lignin obtained industrially by formic acid/acetic acid pulping of wheat straw was used. Environment-friendly, non-toxic polymeric materials of natural origin constitute up to 94% of the total panel binder. The wood panel itself is constituted of 99.5% natural materials, the 0.5% balance being composed of glyoxal, a non toxic and non volatile aldehyde, and of hexamine already accepted as a non-formaldehyde-yielding compound when in presence of condensed tannin. The wood was shown to pass the relevant interior standards with such adhesive formulations.

2.4.3 Production of *Vitis Vinifera* Fiberboards using Lignin

In a study by Mancera et al. (2011), lignin was used as an adhesive to fiberboards. Kraft lignin ranging from 5% to 20% was added to the fiberboards that had been steam-exploded under optimized pre-treatment and pressing conditions. The boards were tested to get the water resistance properties in terms of thickness swelling and water absorption. Physical and mechanical characterization of the boards were also carried to study the modulus of rupture (MOR), modulus of elasticity (MOE) and internal bond (IB). The results showed that there is a decrease of fibreboards water absorption as the percentage of lignin increases. In other words, the water resistance of the boards improved. For mechanical properties, as the lignin increased, the fibreboard also increased in strength. Most notably was that with just 5% of lignin, the strength of the boards were double that of the binderless board. From the studies, they concluded that fiberboards with 15% of lignin had good water resistance and mechanical properties that fulfilled the relevant standard specifications.

2.4.4 Production of Wood using Sodium Hydroxide and Lignin

Young et al. (1985) studied the characteristics of wood surface and made some modification to it by treating it with sodium hydroxide and lignin-formaldehyde or methylolated lignin. Initially, they treated the wood with only sodium hydroxide and found that it can contribute to the wood surfaces strong dry autohesive bonds. However, it has poor water resistance in which they explained that it was due to limited number of secondary hydrogen bonds were formed. Hence, they added methylolated lignin in addition to sodium hydroxide and the end result was that methylolated lignin acted as a reactive gap-filling polymer resulting in excellent dry and wet wood bond strength was obtained. However, there was a need to add an amount of phenol-formaldehyde resin or isocyanate in order to obtain a durable wood bond.

2.4.5 Lignin-phenolformaldehyde Resin Binders

Olivares et al. (1988) studied the copolymerization of lignin with phenol-formaldehyde resin in order to produce adhesives with that has the same characteristics as phenol-formaldehyde resins. They used lignin from *Pinus radiata* black liquor as a copolymer to produce ligninphenol-formaldehyde resin binders. Different modified lignins were tested and resin composed of 18.8% ultrafiltrated high molecular weight lignin, 22.9% phenol and 58.3% formaldehyde had the best mechanical properties and water resistance.